

APPENDIX F

DATA VALIDATION

- **OSI PROGRAM - PHASE 2 - ROUND 1**
- **OSI PROGRAM - PHASE 2 - ROUND 2**

**DATA VALIDATION
OCCIDENTAL CHEMICAL CORPORATION
OFF-SITE INVESTIGATION (OSI)**

Niagara Falls, New York

NOVEMBER 1993

REF. NO. 2583 (DataVal-1)

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CONESTOGA-ROVERS & ASSOCIATES

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1. The first part of the paper discusses the importance of the study area and the objectives of the research. It highlights the need for a comprehensive understanding of the local environment and the impact of human activities on the natural resources.

2. The second part of the paper describes the methodology used in the study. This includes a detailed description of the fieldwork, the data collection methods, and the statistical analysis techniques employed to interpret the results.

3. The third part of the paper presents the results of the study. It includes a series of tables and figures that illustrate the findings of the research. These results are then discussed in the context of the study area and the broader scientific community.

4. The final part of the paper provides a conclusion and discusses the implications of the study. It highlights the key findings and suggests areas for further research. The paper also includes a list of references and an appendix with additional data and figures.

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1.0 EXECUTIVE SUMMARY

Twenty-two (22) groundwater samples (including one field duplicate and one rinsate blank) were collected in May 1993, for the Occidental Chemical Corporation (OxyChem) Off-Site Investigation (OSI) in Niagara Falls, New York. The samples were analyzed for benzene, general organics¹, HPLC parameters, total soluble phosphorous, total organic carbon (TOC), total organic halides (TOX), and various metals.

Benzene

All but two of the benzene results reported were acceptable without qualification. Most samples contained less than 30 µg/L of benzene. Samples OW658C, OW658D and OW659B contained levels of benzene ranging from 840 to 1200 µg/L.

General Organic Parameters

Most sample results were acceptable without qualification. A few positive sample results reported for trichloroethene, tetrachloroethene and 1,2,4-trichlorobenzene were qualified as estimated due to outlying quality control results.

Samples were reported to contain chlorotoluenes, chlorobenzene, dichlorobenzenes, chlorobenzotrifluorides, trichloroethylene, and tetrachloroethylene. The highest concentrations of general organic compounds were observed in samples OW658C, OW658D and OW659B.

HPLC Parameters

All quality control data were acceptable, indicating good accuracy and precision were achieved during sample analysis. All sample results were non-detect.

¹ General Organic and HPLC parameters are listed in Table 2.

Total Soluble Phosphorus

All quality control data were acceptable, indicating good accuracy and precision were achieved during sample analysis. Some phosphorous was detected in samples OW652B, OW653B, OTW653C, OW653D, OW657B, OW657D and OW659D.

TOC

TOC results were not available for sample OW653B as it was received broken at the laboratory. Due to some variability in the Quality Assurance/Quality Control (QA/QC) data, all sample results were qualified as estimated. Positive TOC results ranged from 3 to 18 mg/L.

TOX

Upon review of the TOX data, several deficiencies in the execution of the method were observed. The most critical of these deficiencies was that column breakthrough exceeded the 10 percent limit established in Method 450.1. Due to the uncertainty of the resulting data, all TOX results were qualified as unusable (R).

The deficiencies have been addressed by the laboratory and corrective measures are being implemented to ensure the quality of future TOX analysis.

Metals Analysis

All quality control data provided for arsenic, lead and mercury analyses were acceptable indicating good accuracy and precision were achieved.

All arsenic results were non-detect. Mercury concentrations ranging from 0.7 to 3.1 µg/L were observed in samples

OW650D, OW652D and OW659B. Lead results ranging from 35 to 150 µg/L were reported for samples OW660, OW659D, BH11D-92 and MW-1.

2.0 GENERAL

Analytical services for Occidental Chemical Corporation (OxyChem) were provided by Recra Environmental Incorporated (Recra), Wadsworth/Alert Laboratories (WAL), OxyChem Technology Center - Central Sciences and the OxyChem Niagara Plant Works Laboratory.

Twenty-two (22) groundwater samples (including one field duplicate and one rinsate blank) were collected in May 1993 for the OSI. A sample key is presented in Table 1. The samples were submitted to the above laboratories for the following analyses:

<i>Parameter</i>	<i>Analytical Method</i>
Benzene	USEPA SW-846 Method 8020
General Organics ¹	Occidental Chemical Corporation Microextraction Method
HPLC Parameters ¹	Modified Solvent Exchange Method
Total Soluble Phosphorous	40 CFR Part 136 Method 365.2
Total Organic Carbon (TOC)	USEPA SW-846 Method 9060
Total Organic Halides (TOX)	USEPA Method 450.1 (Modified)
Arsenic and Lead	USEPA Method 200.7
Mercury	USEPA SW-846 Method 7470

The above methods are referenced from sources as detailed in "Appendix C - Chemical Sampling and Quality Assurance Plan, Niagara Plant Supplemental Data Collection Program", May 9, 1988 hereinafter referred to as the "QAP".

A summary of the analytical results is presented in Table 3. The Quality Assurance/Quality Control (QA/QC) criteria by which these data have been assessed are outlined in the QAP.

¹ General Organic and HPLC Parameters are listed in Table 2.

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3.0 HOLDING TIMES

Sample holding times as specified in the relevant methods and the "QAP" are summarized in Table 4. Adherence to these holding time criteria was evaluated by comparison of collection and extraction (and/or analysis) dates obtained from the Chain of Custody forms and final analytical reports respectively. A summary of all sample holding times is attached as Table 5.

Benzene analysis was performed on samples OW653B and OW653D outside of the seven day holding time cited in both the "QAP" and Method 8020. In general, holding time exceedances tend to demonstrate a low bias in results due to the potential loss of the analyte of concern. The associated benzene results were therefore qualified as estimated (see Table 6).

Samples analyzed for arsenic and lead were in exceedance of the 28 day holding time cited in the "QAP". Since these samples were analyzed within the 6 month holding time specified in EPA Method 200.7, however, the data were not qualified.

4.0 SAMPLE PRESERVATION

Upon review of the field log notebooks and sample Chain of Custody forms, it was determined that all samples were properly preserved after collection. All samples were received by the laboratory at 4°C ($\pm 2^\circ\text{C}$), indicating proper storage of samples during shipment.

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5.0 METHOD BLANK ANALYSES

The purpose of assessing the results of laboratory blank analyses is to determine the existence and magnitude of contamination introduced during analysis. Laboratory blanks were analyzed at a minimum frequency of one per 20 investigative samples and/or one per analytical sequence. A summary of the method blank analyses data is presented in Table 7.

TOC values ranging from 1 to 2 mg/L were reported for three of the six blanks analyzed. All sample concentrations less than five times the associated blank concentration were qualified as non-detect, as these results are probably a reflection of laboratory contamination (see Table 8). Blank analyses for all other parameters yielded non-detect results, indicating that laboratory contamination was not a factor for these analyses.

6.0 SURROGATE SPIKE RECOVERIES

In accordance with Method 8020, all samples and blanks analyzed for benzene are spiked with surrogate prior to analysis. Surrogate recoveries provide a means to evaluate the effects of individual sample matrices on analytical efficiency. Control limits for acceptable surrogate recoveries are specified in the "QAP" as 50 to 120 percent.

The surrogate compound employed for VOC analysis was alpha, alpha, alpha-trifluorotoluene, and a summary of the surrogate recoveries is presented in Table 9. Surrogate recoveries could not be reported for samples OW652C, OW652D, OW657B, OW657C and OW657D due to sample matrix interferences. Thus, analytical efficiency could not be evaluated for these sample on the basis of surrogate recoveries.

Benzene analysis of samples OW658B and PASNY139 yielded no surrogate recoveries which indicate a severe problem with analytical efficiency, possibly due to sample matrix effects. Benzene results reported for these two samples were qualified as estimated (qualifier "J") and are summarized below:

<i>Sample I. D.</i>	<i>Analyte (µg/L)</i>	<i>Qualified Sample Conc. (µg/L)</i>
OW658B	Benzene	10J
PASNY139	Benzene	5J

Outlying (high) surrogate recoveries were reported for samples OW652B and MW-1. Potentially, this could indicate a high bias on all positive VOC data for these samples. Since benzene was reported as ND for both samples, however, qualification of the data was not necessary.

The analysis of all remaining samples yielded surrogate spike recoveries within the contract control limits. Laboratory performance was deemed acceptable on an individual sample basis, with the exceptions noted above.

7.0 BLANK SPIKE ANALYSES

Blank spikes are prepared and analyzed as samples to assess the analytical efficiencies of the methods employed, independent of sample matrix effects. Blank spike analyses are performed at a minimum frequency of one per 20 investigative samples, or one per analytical batch. Control limits for acceptable spike recoveries are specified in the "QAP" as 60 to 100 percent, however, recoveries up to 120 percent were considered acceptable.

Blank spikes were reported for the analyses of general organic and HPLC parameters, and a summary of the results is presented in Table 10. Some of the spike recoveries reported for various general organic compounds were outside of the control limits on the low side. This could indicate either a low bias in the calibration of the instrument or an inefficiency in the extraction of these compounds during preparation. Further review of associated reference standard and matrix spike recovery data was necessary to accurately assess the cause of these low recoveries, and is detailed in the following paragraphs.

The blank spike extracted on May 11, 1993 and analyzed on May 12, 1993 yielded low recoveries for trichloroethylene, tetrachloroethylene, 2-chlorobenzotrifluoride, 3,4-dichlorobenzotrifluoride and 2,4-dichlorobenzotrifluoride. The reference standard analyzed on May 12, 1993 yielded acceptable recoveries for all of the above compounds except for 1,2,4-trichlorobenzene which was below the control limits at 58 percent. The calibration of the instrument was therefore acceptable with the one exception. The analysis of the matrix spike and matrix spike duplicate samples extracted on May 11, 1993 yielded low recoveries for all of the above compounds. On this basis, it was concluded that there was inefficiency in the extractions performed on May 11, 1993 and all associated sample results for these compounds were qualified as estimated (see Table 11). Because the blank spike recoveries were only slightly outside of the control limits, however, ND values were deemed acceptable for the intended use of the data without qualification.

The blank spike extracted on May 12, 1993 and analyzed on May 13, 1993 yielded a low recovery for hexachlorocyclopentadiene. The reference standard analyzed on May 13, 1993 yielded an acceptable recovery for this compound indicating acceptable instrument calibration. The matrix spike and matrix spike duplicate samples extracted on May 12, 1993 both yielded acceptable recoveries for this compound indicating acceptable extraction efficiency. As the blank spike result appears to be anomalous, qualification of the data was not deemed necessary.

All other blank spike analyses for both general organic and HPLC parameters were within the control limits, indicating acceptable analytical efficiency was achieved.

8.0 REFERENCE STANDARD ANALYSES

In order to evaluate the accuracy of instrument calibration, reference standards are obtained from an independent source and analyzed. Reference standard analysis is performed at a minimum frequency of one per 20 investigative samples, or one per analytical batch. Reference standards were analyzed for general organics, arsenic and lead, and TOC analyses and the results are summarized in Table 12.

Control limits specified in the "QAP" for the analysis of general organics reference standards were 60 to 100 percent. Again, recoveries up to 120 percent were deemed acceptable. All reference standards recoveries were within these limits except for the reference standard analyzed on May 12, 1993 for general organic compounds. As previously stated, the recovery for 1,2,4-trichlorobenzene was below the control limits indicating a possible problem with instrument calibration. Positive results reported for this compound in all samples analyzed on May 12, 1993 were qualified as estimated (see Table 13). Because the reference standard recovery was only slightly outside the control limits, ND values were deemed acceptable for the intended use of the data without qualification.

The recovery for hexachlorobenzene was 121 percent which is above the upper control limit of 120 percent. Since all sample results for this compound were non-detect, however, qualification of the data was not necessary.

All reference standard analyses for TOC, arsenic and lead yielded recoveries within generally acceptable limits of 80 to 120 percent. Thus acceptable instrument calibration was achieved for these analyses.

9.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSES

The recoveries of MS/MSD analyses are used to assess the analytical accuracy achieved on individual sample matrices. The relative percent difference (RPD) values between the MS and MSD results are used to assess analytical precision. MS/MSD analyses were performed at a minimum frequency of one per 20 investigative samples for benzene, general organic and HPLC parameters. MS/MSD recoveries and RPDs are summarized in Table 14. As established in the "QAP", control limits for percent recovery were 60 to 100 percent (although, for data validation purposes, an upper control limit of 120 percent was employed) and a maximum RPD value of 20 percent was considered acceptable.

All MS/MSD recoveries and RPD values reported for the HPLC and benzene analyses were acceptable based on the criteria stated above. On this basis, analytical accuracy and precision were deemed acceptable for these analyses. Various MS/MSD results reported for the general organics analysis, however, were outlying as detailed in the following paragraphs.

Due to high trichloroethylene content in the samples, MS/MSD recoveries could not be reported for sample OW657C and PASNY139. Accuracy and precision of the trichloroethylene analyses performed on these samples could not be evaluated.

For sample OW657C, the MSD recoveries reported for tetrachloroethylene, 2-chlorobenzotrifluoride and 2,4-dichlorobenzotrifluoride were below the control limits. Since the recoveries reported for these compounds in the MS were acceptable, however, qualification of the data was not deemed necessary. Due to the low tetrachloroethylene recovery reported for the MSD, the resulting RPD was 43 percent. Analytical precision for this compound was not qualified on this basis alone, due to the possibility that the MSD recovery was in error, but overall analytical precision was further assessed in the evaluation of field duplicate samples (see Section 12.2).

Analysis of both the MS and MSD for sample PASNY139 yielded low recoveries for tetrachloroethylene. The tetrachloroethylene result reported for this sample was therefore qualified as estimated due to a potential low bias.

As previously noted in Section 6.0, analysis of the MS and MSD for sample OW652B yielded low recoveries for several compounds. All associated sample data were previously qualified as estimated.

Analysis of the MS for sample OW658B yielded a low recovery for Mirex. Since the MSD recovery reported for this compound was acceptable, however, qualification of the data was not necessary. The RPD reported for 1,2,4,5-tetrachlorobenzene was 25 percent, which is above the limit of 20 percent established in the "QAP". Since all other RPD values reported for this compound were within the control limits, sample data were not qualified on the basis of this outlying RPD. Overall analytical precision was further assessed in the evaluation of field duplicate samples (see Section 12.2).

10.0 MATRIX SPIKE (MS) ANALYSES

The recoveries of MS analyses are used to assess the analytical accuracy achieved on individual sample matrices. Matrix spikes were performed at a minimum frequency of one per 20 investigative samples for metals, phosphorous, and TOC analyses. Recoveries are summarized in Table 15.

All MS recoveries were evaluated against control limits of 75-125 percent. All recoveries were acceptable and thus analytical accuracy was deemed acceptable for these parameters.

100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200

11.0 DUPLICATE SAMPLE ANALYSES

In order to assess laboratory precision, duplicate samples are prepared and analyzed by the laboratory. Analytical precision is deemed acceptable if resulting RPD values are less than 20 percent for sample values greater than five times the contract required detection limits (CRDLs). For sample results less than five times the CRDL, a control limit of plus or minus two times the CRDL is employed.

For this study, duplicate phosphorous and mercury analyses were performed on samples PASNY139 and OW657, and duplicate arsenic and lead analyses were performed on samples OW657, OW658 and OW653C. A summary of the analytical data and resulting RPDs is presented in Table 16. Since all results for these analyses were non-detect, RPD values were not applicable and analytical precision was deemed acceptable.

12.0 FIELD QA/QC

12.1 RINSATE BLANK ANALYSES

Rinsate blanks are collected and analyzed to evaluate the possibility of cross-contamination introduced during sampling. For this study, a rinse blank was collected and analyzed for all parameters. A summary of the results is attached as Table 17.

TOC analysis of the rinse blank yielded a result of 1 mg/L. All sample results less than five times this concentration were qualified as non-detect due to the likelihood that they reflect contamination. A summary of the qualified data is presented in Table 18. All other analyses yielded non-detect results indicating that contamination introduced during sampling was not a factor in this study.

12.2 FIELD DUPLICATE ANALYSES

In order to assess the analytical and sampling protocol precision, field duplicate samples are collected and submitted "blind" to the laboratory for analysis. Precision is then evaluated based on the RPD values reported.

For this study, the field duplicate samples collected were samples OW650 and OW660. A summary of the field duplicate results and RPD values is presented in Table 19. In accordance with the "QAP", RPD values less than 20 percent were considered acceptable for general organics, benzene and HPLC analyses. For all other analyses, a general limit of 30 percent was employed to evaluate overall precision.

RPD values reported for 1,2-dichlorobenzene and 1,2,4-trichlorobenzene were greater than 20 percent. Since the results were at, or very near the detection limits, however, qualification of the data was not deemed necessary.

13.0 CONCLUSIONS

Based on the assessment detailed in the foregoing, the data produced by WAL, Recra, OxyChem Technology Center - Central Sciences and The OxyChem Niagara Plant Works Laboratory are acceptable with the specific exceptions and qualifications noted herein.

TABLE 1
SAMPLE KEY
PHASE 2 - ROUND 1 OSI SAMPLING
OCCIDENTAL CHEMICAL CORPORATION
MAY 1993

Sample I.D.

BH11D
 MW-1
 MW-3
 OW650D
 OW652B
 OW652C
 OW652D
 OW653B
 OW653C
 OW653D
 OW657B
 OW657C
 OW657D
 OW658B
 OW658C
 OW658D
 OW659B
 OW659C
 OW659D
 OW660
 PASNY139

Well I.D.

BH11D
 MW-3*
 MW-2*
 OW650D
 OW652B
 OW652C
 OW652D
 OW653B
 OW653C
 OW653D
 OW657B
 OW657C
 OW657D
 OW658B
 OW658C
 OW658D
 OW659B
 OW659C
 OW659D
 OW650D (Duplicate)
 PASNY139

Notes:

- * Inappropriate sample IDs were designated for these two wells. Throughout this validation, sample IDs are employed, therefore, sample results for MW-1 actually refer to well MW-3 and sample results reported for MW-3 refer to well MW-2.

TABLE 2
GENERAL ORGANIC AND HPLC PARAMETERS
PHASE 2 - ROUND 1 OSI SAMPLING
OCCIDENTAL CHEMICAL CORPORATION
MAY 1993

General Organics

Toluene
 Chlorobenzene
 2-Chlorotoluene
 4-Chlorotoluene
 1,3-Dichlorobenzene
 1,4-Dichlorobenzene
 1,2-Dichlorobenzene
 2,3-/3,4-Dichlorotoluene
 2,6-Dichlorotoluene
 2,3-/3,4-Dichlorotoluene
 Trichloroethylene
 Tetrachloroethylene
 4-Chlorobenzotrifluoride
 2-Chlorobenzotrifluoride
 3,4-Dichlorobenzotrifluoride
 2,4-Dichlorobenzotrifluoride
 1,2,4-Trichlorobenzene
 1,2,3-Trichlorobenzene
 Hexachlorobutadiene
 2,4,5-Trichlorotoluene
 2,3,6-Trichlorotoluene
 1,2,4,5-Tetrachlorobenzene
 Hexachlorocyclopentadiene
 2,4,5-Trichlorophenol
 1,2,3,4-Tetrachlorobenzene
 Octachlorocyclopentene
 a-Hexachlorocyclohexane
 b-Hexachlorocyclohexane
 Hexachlorobenzene
 g-Hexachlorocyclohexane
 d-Hexachlorocyclohexane
 Perchloropentacyclodene (Mirex)

HPLC Parameters

Benzoic Acid
 2-Chlorobenzoic Acid
 3-Chlorobenzoic Acid
 4-Chlorobenzoic Acid
 Chlorobenzoic Acids, Total
 Chloroendic Acid